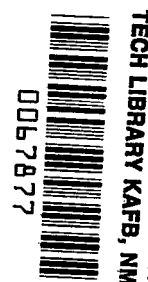


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# Carbon-Catalyzed Oxidation of $\text{SO}_2$ by $\text{NO}_2$ and Air

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## SUMMARY

A series of experiments has been performed using carbon particles (commercial furnace black) as a surrogate for soot particles. Carbon particles were suspended in water and gas mixtures were bubbled into the suspensions to observe the effect of carbon particles on the oxidation of  $\text{SO}_2$  by air and  $\text{NO}_2$ . Identical gas mixtures were bubbled into a blank containing only pure water. After exposure each solution was analyzed for pH and sulfate content. It was found that  $\text{NO}_2$  greatly enhances the oxidation of  $\text{SO}_2$  to sulfate in the presence of carbon particles. The amount of sulfate found in the blanks was significantly less. Under the conditions of these experiments no saturation of the reaction was observed and  $\text{SO}_2$  was converted to sulfate even in a highly acid medium ( $\text{pH} > 1.5$ ).

## INTRODUCTION

Many mechanisms have been proposed for the oxidation of  $\text{SO}_2$  in the atmosphere. These include homogeneous reactions in the gas phase (ref. 1) and heterogeneous reactions in cloud droplets or liquid-phase aerosols (refs. 2 to 4) and on carbon particles (refs. 5 and 6). In order to assess the relative contribution of the various mechanisms and to propose enlightened control strategies, the competing processes must be evaluated in detail.

The work described here addresses one aspect of this problem, namely heterogeneous oxidation of  $\text{SO}_2$  by air and  $\text{NO}_2$  on carbon (soot) particles suspended in water. Similar reactions are possible in the atmosphere in liquid droplets or aerosols containing insoluble carbon particles. Novakov et al. (ref. 5) have established that soot is effective in oxidizing  $\text{SO}_2$  to sulfate in the presence of  $\text{O}_2$ . Carbon particles are found even in remote areas such as the Arctic (ref. 7) and are virtually ubiquitous. Therefore they are widely available to provide reactive sites.

The experiments involving carbon suspended in liquid water were prompted by our original experiments performed with dry carbon particles (ref. 8). When such particles were exposed to mixtures of humidified air,  $\text{SO}_2$ , and  $\text{NO}_2$  they became wetted after a certain time, and it was not clear at that point whether solution chemistry was dominant or if the soot still played an important role.

## EXPERIMENTAL PROCEDURE

Carbon particles (commercial furnace black) were suspended in distilled water at a concentration of 100 mg/10 ml, and commercially prepared mixtures of gases (supplier-certified mixtures in ultrahigh-purity carrier) were bubbled into the aqueous suspension. The apparatus is shown schematically in figure 1. The same gas mixtures were also bubbled through 10 ml of pure water to serve as a blank. The gases (100 ppm  $\text{SO}_2$  in air or  $\text{N}_2$  and 100 ppm  $\text{NO}_2$  in  $\text{N}_2$ ) were mixed prior to splitting the flow between the two reaction vessels. The reactors were held at a constant temperature of  $23^\circ\text{C}$  in a water bath. This configuration allowed the blank and the aqueous carbon suspension to be exposed to identical conditions, so that the difference in amount of sulfate produced in the two reactors was a direct measure of the

effect of the carbon. After each experiment the resulting solutions were analyzed for pH and sulfate content using a barium turbidity test (ref. 8).

## RESULTS AND DISCUSSION

The results of several experiments are presented graphically in figure 2. The yield of sulfate under identical exposure conditons is much larger in the presence of the carbon. The carbon acts as a catalyst for the oxidation of  $\text{SO}_2$  by both air and air with 100 ppm  $\text{NO}_2$  added. Apparently the carbon provides sites for the  $\text{SO}_2$  oxidation to occur because, as the blank curves indicate, neither air nor  $\text{NO}_2$  has any significant oxidation effect in water alone. The conversion rate of  $\text{SO}_2$  in air at 100 ppm with 1 percent carbon is 9.3 percent per hour and increases to 58 percent per hour when 100 ppm  $\text{NO}_2$  is added. These results are in agreement with those obtained in previous experiments in this laboratory (ref. 8) in which  $\text{NO}_2$  significantly enhanced the oxidation of  $\text{SO}_2$  on carbon particles. Some enhancement of the oxidation of  $\text{SO}_2$  by  $\text{NO}_2$  has also been observed on dry soot by Britton and Clarke (ref. 9) and on dry  $\text{V}_2\text{O}_5$  by Barbaray et al. (ref. 10).

To distinguish the oxidizing effect of  $\text{NO}_2$  from that of the  $\text{O}_2$  in air, the same experiment was performed with the  $\text{SO}_2$  and  $\text{NO}_2$  mixed in  $\text{N}_2$ . The results are shown in figure 3. Here only the oxidizing capacity of the  $\text{NO}_2$  is measured. The experiments in  $\text{N}_2$  indicate that  $\text{NO}_2$  acts as an oxidizing agent independent of the  $\text{O}_2$  in air, and comparison of results from figures 2 and 3 shows that the effects of  $\text{O}_2$  and  $\text{NO}_2$  are additive. The intercept of 0.64 mg sulfate in figures 2 and 3 was found to be due to sulfate present on the carbon surface as received from the manufacturer.

Several 20-hour runs were made at  $\text{SO}_2$  and  $\text{NO}_2$  concentrations of 100 ppm and flow rates of 100  $\text{cm}^3/\text{min}$  for each gas. The sulfate yields were the same (30 mg) as would be predicted by linear extrapolation of the data in figure 2. This indicates that  $\text{SO}_2$  was converted to sulfate with no observable saturation effect for these long exposures. The pH of the solutions for these runs was as low as 1.5, indicating that the conversion takes place under highly acidic conditions. Saturation effects have consistently been observed for  $\text{SO}_2$  on dry particles by others (refs. 9, 11, and 12), but we have observed no saturation in either the gravimetric or bubbler experiments as long as sufficient  $\text{H}_2\text{O}$  vapor or liquid  $\text{H}_2\text{O}$  is present.

If the 20-hour runs were extrapolated to typical atmospheric  $\text{SO}_2$  concentrations of 0.01 ppm, this would indicate that "wet" soot particles could be exposed for  $2 \times 10^6$  hours without saturation effects. This is certainly much longer than typical particle lifetimes in the atmosphere.

## CONCLUSIONS

The experimental results reported herein lead to the following conclusions:

1. Carbon particles significantly catalyze the oxidation of  $\text{SO}_2$  to sulfate by air and/or  $\text{NO}_2$ .
2.  $\text{NO}_2$  is an effective oxidizer for  $\text{SO}_2$  in aqueous suspensions of carbon and its effect is independent of the presence or absence of air; the reaction is controlled by the  $\text{NO}_2$ , provided sufficient  $\text{SO}_2$  is present.

3. The yield of sulfate in the reactions studied appears to be independent of pH at values as low as 1.5, and no saturation occurs for long exposure times so long as sufficient  $H_2O$  is present.

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March 16, 1982

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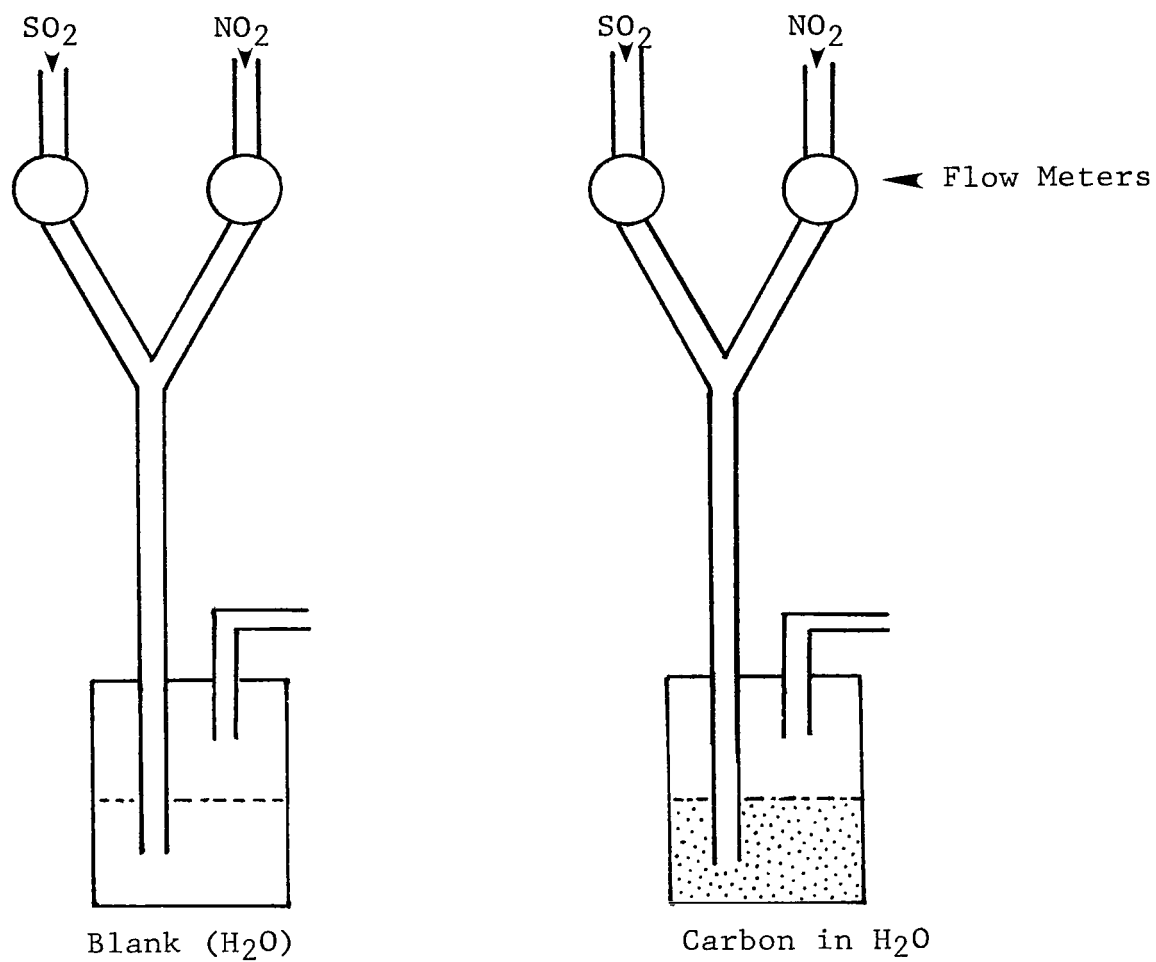


Figure 1.- Apparatus used to investigate  $\text{SO}_2$  oxidation in presence of aqueous carbon suspension.

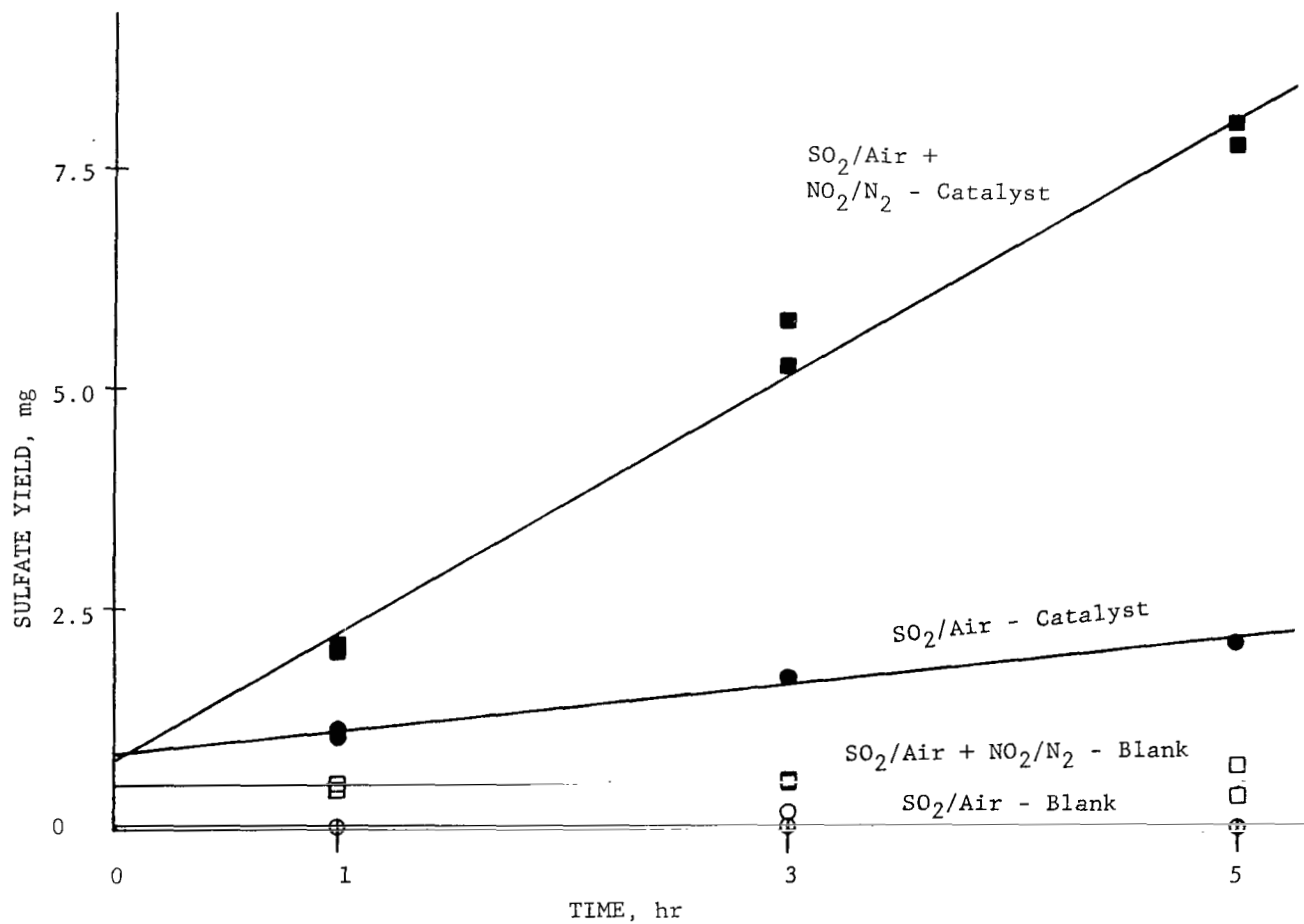


Figure 2.- Effect of NO<sub>2</sub> and catalyst on sulfate yield in air. Blank: 10 ml H<sub>2</sub>O; catalyst: 100 mg carbon black in 10 ml H<sub>2</sub>O; flow rates: 100 cm<sup>3</sup>/min, each gas; concentrations: 100 ppm, each gas.



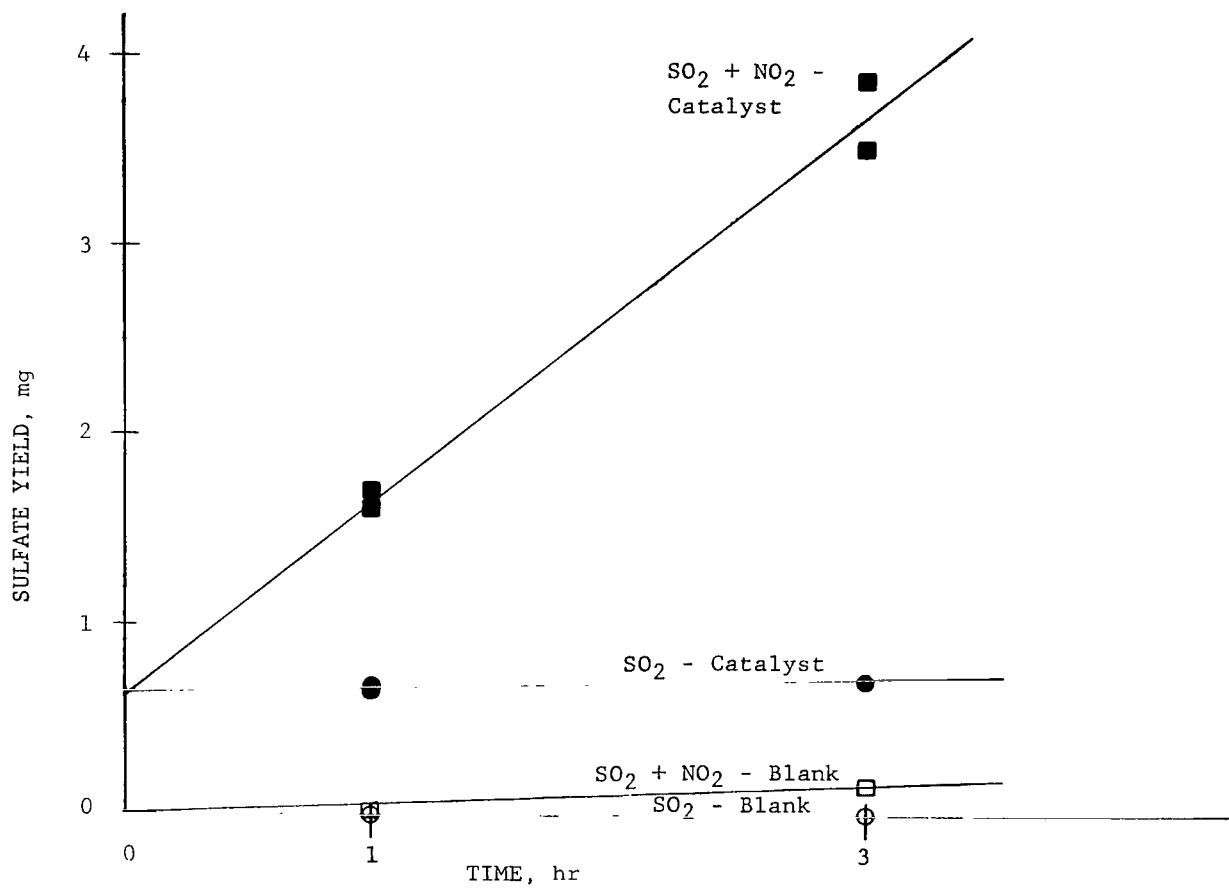


Figure 3.- Effect of NO<sub>2</sub> and catalyst on sulfate yield in N<sub>2</sub>. Blank: 10 ml H<sub>2</sub>O; catalyst: 100 mg carbon black in 10 ml H<sub>2</sub>O; flow rates: 100 cm<sup>3</sup>/min, each gas; concentrations: 100 ppm in N<sub>2</sub>, each gas.

1. Report No. NASA TP-2014		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  CARBON-CATALYZED OXIDATION OF SO <sub>2</sub> BY NO <sub>2</sub> AND AIR				5. Report Date April 1982	
				6. Performing Organization Code 146-20-10-19	
7. Author(s) Robert S. Rogowski, David R. Schryer, Wesley R. Cofer III, Robert A. Edahl, Jr., and Shekhar Munavalli				8. Performing Organization Report No. L-15214	
9. Performing Organization Name and Address  NASA Langley Research Center Hampton, VA 23665				10. Work Unit No.	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address  National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered Technical Paper	
				14. Sponsoring Agency Code	
15. Supplementary Notes  Robert S. Rogowski, David R. Schryer, Wesley R. Cofer III, and Robert S. Edahl, Jr.: Langley Research Center, Hampton, Virginia. Shekhar Munavalli: Livingstone College, Salisbury, North Carolina. This paper also appears in Heterogeneous Atmospheric Catalysis, Geophys. Monogr. Ser., vol. 27, edited by David R. Schryer, AGU, Washington, DC, 1982.					
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17. Key Words (Suggested by Author(s)) Sulfur dioxide Sulfate Carbon Catalysis Acid rain			18. Distribution Statement  Unclassified - Unlimited  Subject Category 25		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 8	22. Price A02		

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